

Project Title: Decoupling Activity and Durability in PEMFC Cathodes via Nanoscale Oxide Engineering

Project Number IMURA1322

Monash Main Supervisor
(Name, Email Id, Phone) A/Prof. Sebastian Thomas,
Sebastian.Thomas@monash.edu *Full name, Email*

Monash Co-supervisor(s)
(Name, Email Id, Phone)

Monash Head of Dept/Centre (Name,Email) Prof. Matthew Hill
Matthew.Hill@monash.edu *Full name, email*

Monash Department: Materials Science and Engineering

Monash ADGR
(Name, Email) A/Prof. Timothy Scott
Timothy.Scott@monash.edu *Full name, email*

IITB Main Supervisor
(Name, Email Id, Phone) Prof. Nagappan Ramaswamy
nagappan@iitb.ac.in *Full name, Email*

IITB Co-supervisor(s)
(Name, Email Id, Phone)

IITB Head of Dept
(Name, Email, Phone) Prof. Mahesh Tirumkudulu
head.che@iitb.ac.in
+91-22-25767200 *Full name, email*

IITB Department:

Research Clusters:

Research Themes:

Highlight which of the Academy's CLUSTERS this project will address? (Please nominate JUST <u>one</u> . For more information, see www.iitbmonash.org)		Highlight which of the Academy's Theme(s) this project will address? (Feel free to nominate more than one. For more information, see www.iitbmonash.org)	
1	Material Science/Engineering (including Nano, Metallurgy)	1	Artificial Intelligence and Advanced Computational Modelling
2	Energy, Green Chem, Chemistry, Catalysis, Reaction Eng	2	Circular Economy
3	Math, CFD, Modelling, Manufacturing	3	Clean Energy
4	CSE, IT, Optimisation, Data, Sensors, Systems, Signal Processing, Control	4	Health Sciences
5	Earth Sciences and Civil Engineering (Geo, Water, Climate)	5	Smart Materials
6	Bio, Stem Cells, Bio Chem, Pharma, Food	6	Sustainable Societies
7	Semi-Conductors, Optics, Photonics, Networks, Telecomm, Power Eng	7	Infrastructure
8	HSS, Design, Management		

The research problem

Proton exchange membrane fuel cells (PEMFCs) rely on Pt-based nanoparticles supported on carbon to catalyse the oxygen reduction reaction (ORR) at the cathode. Despite decades of optimisation, the long-term durability of these catalysts under realistic operating conditions remains a critical barrier to large-scale deployment, particularly for heavy-duty applications requiring lifetimes approaching 30,000 hours. Under acidic conditions and dynamic potential cycling between ~ 0.6 and >1.0 V vs RHE, Pt undergoes repeated oxidation and reduction. Transient high-potential excursions during start–stop events accelerate Pt oxide formation, followed by reductive dissolution during cathodic sweeps. Dissolved Pt species redeposit non-uniformly, promoting Ostwald ripening and particle coarsening, which reduce electrochemically active surface area (ECSA) and mass activity. In Pt-alloy systems such as PtCo, selective dissolution of the less noble alloying element further destabilises the catalyst, altering surface composition, disrupting strain and ligand effects responsible for enhanced ORR kinetics, and releasing transition metal cations into the ionomer and membrane. These dissolved species interact with perfluorosulfonic acid (PFSA) ionomers, exchange with proton sites, and degrade membrane conductivity, thereby coupling catalyst degradation directly to cell-level voltage losses [Ramaswamy *et al.*, *Journal of the Electrochemical Society*, 2025].

Efforts to improve durability through alloy optimisation, intermetallic ordering, and carbon support engineering have achieved incremental gains but have not fundamentally suppressed metal dissolution under high-potential cycling. Moreover, improvements in intrinsic activity often exacerbate stability issues, and aggressive Pt thrifting

reduces tolerance to dissolution-induced ECSA loss. The central limitation is that current catalyst architectures expose Pt surfaces directly to the acidic electrolyte and ionomer environment, where electrochemical oxidation, metal–sulfonate interactions, and carbon corrosion proceed concurrently [Ramaswamy *et al.*, *Journal of the Electrochemical Society*, 2025]. A strategy that stabilises the catalyst–electrolyte interface without compromising transport or kinetics is therefore required.

Ultra-thin metal oxide coatings—on the order of sub-nanometre to a few nanometres—have emerged as a promising approach to mitigate these degradation pathways. Conformal oxide layers deposited via nanofabrication techniques or controlled surface oxidation can, in principle, suppress Pt dissolution by modifying the interfacial redox thermodynamics, limiting direct exposure of alloying elements to the electrolyte, and reducing metal–ionomer coordination. Such coatings may also act as physical barriers to nanoparticle migration, thereby inhibiting coalescence and support detachment. However, the introduction of oxide films introduces a fundamental multi-physics trade-off. Oxides are typically less electronically conductive than metallic Pt, and even ultrathin layers may impose kinetic barriers to electron transfer, alter ORR adsorption energetics, or increase oxygen transport resistance. Proton transport through dense oxide layers may be limited, and structural instability of the coating under repeated potential cycling could lead to cracking, delamination, or gradual loss of protective function. Furthermore, the electrochemical stability window of candidate oxides in strongly acidic environments at potentials approaching 1.2 V vs RHE is not fully understood.

The core research problem is therefore to establish the mechanistic and design principles governing ultra-thin metal oxide coatings that can simultaneously suppress Pt and alloy-metal dissolution, prevent membrane contamination, and preserve ORR activity and mass transport under realistic PEMFC operating conditions. This requires elucidating how oxide composition, thickness, defect structure, and electronic properties influence interfacial charge transfer, oxygen permeability, and proton accessibility, as well as how these parameters evolve during long-term potential cycling. A quantitative framework linking nanoscale interfacial chemistry to catalyst-layer transport and cell-level performance is currently lacking. Addressing this gap will enable the rational design of oxide-stabilised cathode catalysts that decouple durability from performance penalties, advancing PEMFC technology toward cost-effective and long-lived heavy-duty operation.

Project aims

Mechanistic Understanding of Dissolution Suppression

To determine how ultra-thin metal oxide coatings influence Pt oxidation–reduction driven dissolution and selective alloy dealloying under realistic PEMFC potential cycling. This aim will quantify metal dissolution kinetics and establish how oxide thickness, composition, and defect structure modify interfacial redox behaviour and ECSA loss mechanisms.

Impact of Oxide Coatings on ORR Kinetics and Transport

To evaluate how conformal oxide layers affect oxygen reduction reaction activity, charge transfer, oxygen permeability, and proton accessibility. The objective is to identify coating parameters that suppress degradation without introducing significant kinetic or mass transport penalties in catalyst layers

Long-Term Stability and MEA-Level Performance

To assess the structural integrity and electrochemical stability of oxide-coated catalysts under extended potential cycling and high-potential excursions. This aim will correlate nanoscale coating evolution with ECSA retention, membrane contamination, and overall fuel cell performance to establish practical design rules for durable cathodes.

How skills/experience of the IITB and the Monash supervisor(s) support the proposed project

A/Prof. Sebastian Thomas is an expert in electrochemistry and materials degradation, with extensive experience in metal dissolution, interfacial reactions, and hydrogen–metal interactions under electrochemical conditions. His expertise in mechanistic electrochemistry and reaction–transport modelling will provide critical guidance in understanding the redox-driven dissolution of Pt and alloying elements under high-potential PEMFC operating conditions. He will contribute to the design of electrochemical protocols that simulate start–stop and load-cycling environments, enabling quantitative assessment of metal ion release, interfacial stability, and degradation kinetics.

Prof. Nagappan Ramaswamy is an internationally recognised expert in PEM fuel cell electrocatalysis, with particular expertise in Pt-based cathode catalysts, catalyst-layer architecture, and degradation mechanisms under realistic operating conditions. He will provide guidance on the rational design and evaluation of ultra-thin oxide-stabilised Pt catalysts, including mechanistic insights into Pt and alloy-metal dissolution, ionomer–catalyst interactions, and performance losses under potential cycling.

What is expected of the student when at IITB and when at Monash?

At IIT Bombay, the student would be expected to:

Perform synthesis and characterisation of PEMFC cathodes and trial new thin film coatings on PEMFC cathodes.

At Monash, the student would be expected to:

Perform mass spectroelectrochemistry measurements on PEMFC cathodes in acidic solutions and use nanofabrication methods to deposit metal oxide coatings on PEMFC cathodes.

Expected outcomes

Mechanistic Framework for Oxide-Stabilised Pt Catalysts

The project will deliver a quantitative mechanistic understanding of how ultra-thin metal oxide coatings modify Pt oxidation–reduction behaviour, suppress alloy-metal dissolution, and influence nanoparticle stability under realistic potential cycling. This framework will link interfacial electrochemistry to structural evolution and ECSA retention.

Optimised Oxide Coating Design Parameters

The research will establish clear design rules relating oxide composition, thickness, and electronic properties to ORR activity, oxygen/proton transport, and long-term durability. These guidelines will define the optimal coating window that decouples dissolution suppression from kinetic and mass transport penalties.

Demonstration of Enhanced MEA Durability

The project will demonstrate oxide-coated Pt-based cathodes with significantly improved ECSA retention and reduced membrane contamination under accelerated stress testing, validating the strategy at the membrane electrode assembly level and advancing PEMFC systems toward heavy-duty durability targets.

How will the project address the Goals of the above Themes?

This project aligns strongly with **Clean Energy** by addressing durability and cost barriers in PEM fuel cells, a key technology for hydrogen-powered, zero-emission transport. By extending catalyst lifetime and reducing platinum dependence, the research supports scalable, low-carbon energy systems and sustainable heavy-duty mobility.

It aligns with **Smart Materials** through the rational design of ultra-thin, functional oxide coatings that actively stabilise Pt nanoparticles under dynamic electrochemical conditions. These engineered interfacial layers are tailored to simultaneously control dissolution, transport, and catalytic activity, exemplifying multifunctional, adaptive materials design at the nanoscale.

How well the IITB and the Monash supervisor(s) know each other

A/Prof. Sebastian Thomas and Prof. Nagappan Ramaswamy have worked together

Potential RPCs from IITB and Monash

From IITB:

1. Prof. Vijayshankar Dandapani – expert in electrochemistry
2. Prof. Karthikeyan Hariharan- expert in corrosion and high temperature oxidation of materials

From Monash:

1. Dr. Victor Cruz de Faria (expert in corrosion)

Capabilities and Degrees Required

Degree in Metallurgy, or Materials Science, or Chemistry, or Electrochemistry or Chemical Engineering.
Ability to perform electrochemical experiments will be preferred

Necessary Courses

Name three tentative courses relevant to the project that the student should complete during his/her coursework at IITB (the student will require to secure 8 point in these courses)

Aqueous corrosion

Electrochemistry

Materials characterisation: XRD or electron microscopy

Potential Collaborators

Please visit the IITB website www.iitb.ac.in OR Monash Website www.monash.edu to highlight some potential collaborators that would be best suited for the area of research you are intending to float.

At IITB

1. Prof. Vijayshankar Dandapani

At Monash:

2. Yuxiang Wu

Keywords relating to this project to make it easier for the students to apply.

Fuel cells, Pt catalyst, durability, Pt dissolution, PEMFC cathode